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An X-ray study of the Dzyaloshinskii-Moriya interaction in the weak ferromagnet $FeBO_3$

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Abstract. We report on the axis, magnitude and direction of the Dzyaloshinskii-Moriya (DM) interaction in the weak ferromagnet $FeBO_3$. The latter relies on the determination of the phase of the magnetic x-ray scattering amplitude. We outline a new technique based on interference with forbidden quadrupole resonant scattering to obtain this phase information.

1. Introduction

Weak ferromagnetism in materials such as $\alpha-Fe_2O_3$ was cited by Moria [1] as being '*a controversial problem for a decade*' back in 1960, and played a crucial role in the development of the theory of antisymmetric exchange (Dzyaloshinskii-Moriya) interactions. In recent years interest has shifted towards other manifestation of the DM interaction, such as the magnetoelectric effect [2] and skyrmion states [3], where reliable theoretical predictions have been lacking. Weak ferromagnets provide an excellent test-bed for theories due to the fact that the twisting of the atomic moments is purely local and leads to a small and manageable magnetic unit cell, in contrast to the long-period modulations observed in globally chiral crystals. Unfortunately, while the local nature of the twisted moments is highly beneficial for theoretical development, it leads to some severe experimental challenges. Most notably, it is necessary to extract the *phase* of the magnetic scattering, rather than the usual intensity.

In this paper, we present a study of the weak ferromagnet $FeBO_3$. We discuss the direction (axis) of the DM interaction by considering its symmetry, and the magnitude of the interaction via the canting angle. Most significantly, we show the first results from a novel interference technique proposed by some of us [4] to determine the phase of the magnetic x-ray scattering signal, and the sign of the DM interaction in $FeBO_3$.

2. Dzyaloshinskii-Moriya Interaction and Symmetry

The most general form of the bilinear coupling energy between two spins, $\mathbf{S}^1$ and $\mathbf{S}^2$ (S_i^1 and S_j^2 in Cartesian tensor component form) can be written as the contraction of a second-rank tensor M_{ij} with the spins to form a phenomenological classical spin Hamiltonian,

$$\Delta E = S_i^1 \, S_j^2 \, M_{ij} \tag{1}$$

Here, the nine components M_{ij} can be expressed as a scalar (one component), a symmetric traceless tensor (five components) and an antisymmetric tensor (three components):

$$\Delta E = J S_i^1 \, S_j^2 \, \delta_{ij} + S_i^1 \, S_j^2 \, M_{ij}^S + S_i^1 \, S_j^2 \, M_{ij}^A \tag{2}$$

Of these three terms, the isotropic part always dominates and the symmetric anisotropic term is small enough that it can typically be neglected. The third term (antisymmetric part) is the $Dzyaloshinskii - Moriya$ interaction, which is similarly small but plays a crucial role in the canting of the spins. The isotropic and antisymmetric parts can be written equivalently in terms of scalar and vector products of the spins, respectively:

$$\Delta E = J \mathbf{S}^1 \cdot \mathbf{S}^2 + \mathbf{D} \cdot [\mathbf{S}^1 \times \mathbf{S}^2] \tag{3}$$

Table 1. The Moriya Rules [1] that govern the DM vector, $\mathbf{D}$, between two spins at points A and B with a mid-point at C, and a comment on whether these are consistent with $\mathbf{D}$ transforming as a polar or axial vector

Moriya Rule	Polar?	Axial?
1. When a center of inversion is located at C, $\mathbf{D} = \mathbf{0}$	yes	no
2. When a mirror plane perpendicular to AB passes through C, $\mathbf{D} \parallel$ mirror plane or $\mathbf{D} \perp AB$	yes	no
3. When there is a mirror plane including A and B, $\mathbf{D} \perp$ mirror plane	no	yes
4. When a two-fold rotation axis perpendicular to AB passes through C, $\mathbf{D} \perp$ two-fold axis	no	no
5. When there is an n-fold axis ($n \geq 2$) along AB, $\mathbf{D} \parallel AB$	yes	yes

If we consider the strength of the coupling between spins to be a physical property of the crystal then $\mathbf{D}$ might be expected to possess the symmetry of the environment in which it acts, specifically, the site-symmetry of the point mid-way between the coupled spins. As $\mathbf{D}$ is clearly a vector, one might then ask whether it transforms as a polar or axial vector. Indeed, Moriya studied the symmetry of the antisymmetric exchange interaction in a seminal paper [1] that introduced five celebrated 'Moriya rules'. We reproduce those rules in Table 1 and ask, for each, whether the rule is compatible with a polar or axial vector. Interesting, we see that no clear pattern emerges: it appears that $\mathbf{D}$ does not transform as a vector at all!

The difficulty arises from the fact that our Hamiltonian neglects the vector that links the positions of the two spins - an omission that is critical due to the fact that the positions of the spins is reversed by some symmetry operations. Dmitrienko et al. [4] argued that to describe the DM coupling with correct transformation properties, one must introduce a third-rank tensor, which couples to the two spins as well as the vector linking them:

$$\Delta E = T_{ijk} \, S_i^1 \, S_j^2 \, \hat{r}_k^{12} \tag{4}$$

from which the DM 'vector' can be obtain from

$$D_n = \frac{1}{2} \varepsilon_{ijn} \, T_{ijk} \, \hat{r}_k^{12} \tag{5}$$

where ε_{ijn} is the permutation tensor. As an indication that such a procedure is not unreasonable, one can apply the symmetries highlighted by the Moriya rules. In all five cases the representation developed by Dmitrienko et al. reproduce the results of Moriya. Moreover, from Eqn. 5 one can obtain the sixth Rule omitted by Moriya: vector $\mathbf{D}$ is directed along $\hat{\mathbf{r}}^{12}$ when there is

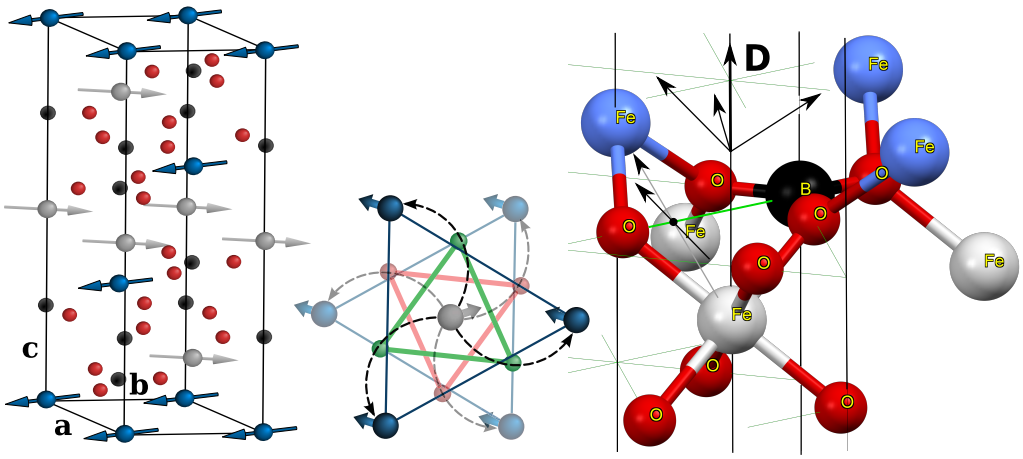

Figure 1. Magnetism in $FeBO_3$ (spacegroup $R\bar{3}c$). Left: a magnetic (hexagonal) unit cell, showing oxygen atoms (red), boron atoms (black), and two symmetry-related magnetic iron sublattices (blue and grey) with moments tilted in the ab plane between the two. Right: DM vectors. The vector linking two neighbouring irons is shown in grey, with a two-fold axis (green) passing through its mid-point (black dot). The fourth Moriya rule dictates that the DM vector (thin black arrow) must be perpendicular to the two-fold axis. The resultant DM vector linking the two sublattices (thick black arrow) is the sum of individual vectors, which are related by three-fold rotation along c (thin back lines), and therefore points along the three-fold axis. Centre: The twisting of oxygen atoms and magnetic spins, going up (green oxygens, dark blue iron atoms) and down (pink oxygens, light blue iron atoms) from the central iron atom, looking into the c axis.

an n-fold ($n \geq 3$) axis perpendicular to $\hat{\mathbf{r}}^{12}$ (i.e. vector $\mathbf{D}$ is normal to the n-fold axis - a somewhat counterintuitive result!). For example, if two spins interact through a chiral liquid then, according to spherical symmetry of liquid, $T_{ijk} \propto \varepsilon_{ijk}$ and $\mathbf{D} \parallel \hat{\mathbf{r}}^{12}$.

Having established that the transformation properties of the third-rank DM *tensor* reproduce the Moriya rules, one can carry out the necessary symmetrization for the site symmetry of all mid-points between neighbouring magnetic ions in order to establish (a) whether or not the DM interaction is allowed and (b) any symmetry constraints on its orientation. In the case of $FeBO_3$, the nearest iron atoms (one from each sublattice) have at their mid-point a non-centrosymmetric site, allowing in principle the possibility of the DM interaction. Moreover, a two-fold axis, perpendicular to the two iron atoms passes through the midpoint. Moriya Rule No. 4 states that $\mathbf{D}$ must therefore act perpendicular to the two-fold axis (Fig. 1). Finally, summing over all symmetry-equivalent $\mathbf{D}$ vectors that act between the two iron sublattices, three fold rotation symmetry about the c axis ensures that the resultant $\mathbf{D}$ vector is parallel to c. A DM vector along c is consistent with the proposed magnetic structure: from Fig. 1 we see that the vector product of a spin from each sublattice is directed along c.

3. The Magnitude of the Dzyaloshinskii-Moriya Interaction

The DM interaction is weak compared to the isotropic exchange, meaning that the magnetic structure of $FeBO_3$ is essentially antiferromagnetic, with sublattices almost antiparallel and a small twist leading to *weak* ferromagnetism. The classical spin Hamiltonian in Eqn. 3 can then be re-written in terms of the canting angle (ϕ) between sublattice,

$$\Delta E \propto -J\cos(2\phi) + D\sin(2\phi). \tag{6}$$

As this state must correspond to an energy minimum we can set its derivative to zero to obtain

$$\frac{D}{J} = -\tan(2\phi) \simeq -2\phi \tag{7}$$

The value of the isotropic exchange, obtained by Mössbauer spectroscopy, and the magnitude of the canting angle determined by magnetization measurements, are J=7.5 meV and $|\phi|$= 0.016 rad. respectively [5]. Inserting these values into Eqn. 7 gives the magnitude of the DM vector to be $|D|$=0.24 meV.

4. The Sign of the Dzyaloshinskii-Moriya Interaction

At this point, we already know *almost* everything about the DM vector: we know its magnitude, and we know that it lies parallel to the crystal c axis. What we *don't* know is whether the DM vector linking adjacent sublattices points up or down. That is, we don't know the sign of the DM-vector, i.e. whether the magnetic twist follows the twist of the oxygen atoms between magnetic ions or opposes it.

The standard techniques for determining the arrangement of atomic spins in a crystal are x-ray and neutron diffraction. Assuming that orbital polarization is extremely small, the structure factor for the non-resonant magnetic $(hkl) = (0, 0, 6n + 3)$ reflections can be written [6] as,

$$\mathbf{F}_{\text{spin}}(\mathbf{Q}) = 2Sf_S(\mathbf{Q})\frac{\mathbf{H} \times \mathbf{D}}{|\mathbf{H}||\mathbf{D}|} \tag{8}$$

where S is the total spin of the iron atom, $f_S(\mathbf{Q})$ is the spin form factor, and $\mathbf{H}$ is the direction of a weak external field, strong enough to rotate the ferromagnetic component into the field direction. This expression shows that the magnetic structure factor, which is determined by the antiferromagnetism, is perpendicular to $\mathbf{H}$ as one would expect from Fig. 1. The ability to rotate the antiferromagnetic structure via an external field is extremely attractive as it allows structure factor vector directions to be determined without physically rotating the crystal in an 'azimuthal' scan. However, since the scattered intensity $I \propto |\mathbf{B} \cdot \mathbf{F}_{\text{spin}}(\mathbf{Q})|^2$, there is an obvious problem: the sign of $\mathbf{D}$ reverses the phase of the magnetic scattering but does not affect its intensity. (Here, vector $\mathbf{B}$ depends on the polarization and wave vectors of incident and scattered beams; for the $\sigma - \pi$ channel used in our experiments, $\mathbf{B}_{\sigma\pi} = \mathbf{k}(1 - \mathbf{k} \cdot \mathbf{k}')$).

In order to determine the phase of the magnetic scattering and hence the sign of the DM interaction, it is necessary to carry out some kind of interference measurement. It was pointed out by Dmitrienko et al. [4] that in $FeBO_3$, and indeed a surprisingly wide range of other weak ferromagnets, there is a fortuitous overlap between magnetic diffraction and pure quadrupole resonant forbidden x-ray scattering, of the type first reported by Finkelstein et al. [7]. The latter is only slightly stronger than the magnetic scattering and occurs at almost a single sharp resonance in the iron K pre-edge region. The scattered intensity is now given by $I \propto |\mathbf{B} \cdot \mathbf{F}_{\text{spin}}(\mathbf{Q}) + F(E2E2)|^2$ where $F(E2E2)$ is the pure quadrupole scattering amplitude. Moreover, despite it's apparently exotic nature, $F(E2E2)$ is very well understood and accurately modeled by theoretical codes such as FDMNES [8] and thus provides a reliable 'reference wave' for an interference experiment.

Experiments were carried out at XMaS (BM-28) at the ESRF, and I16 at Diamond Light Source. In both cases the sample was attached to a cryofurnace, mounted on a large six-circle diffractometer. At I16, measurements were made of the 003 forbidden reflection close to resonance, revealing a single sharp resonant peak that is aligned with the pre-edge feature of the fluorescence spectrum (Fig. 2, left), as is typical for pure quadrupole resonant reflections. Measuring far from resonance allowed observation of the much weaker pure magnetic reflection, also at the 003 position, originating from the antiferromagnetic modulation of the iron moments.

The magnetic motif was rotated by a small (0.011 T) external field to produce a very high quality 'azimuthal' type scan, with a shape that is consistent with pure spin scattering (Fig. 2, right). It is worth noting that, the high quality of the data obtained via this technique is due mainly to the fact that the sample azimuthal angle is fixed and so no multiple scattering conditions are excited during the measurement.

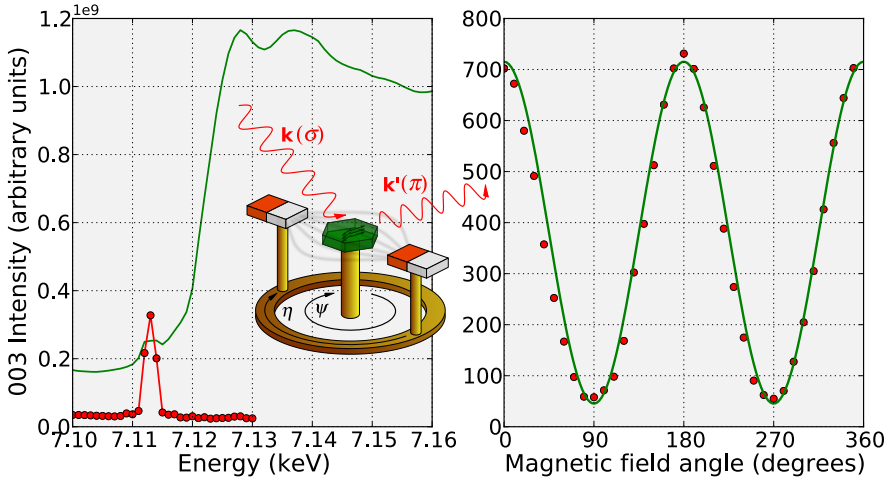

Figure 2. Left: Fluorescence (green line), and the 003 resonant diffraction spectra (red lines and circles) showing a single sharp peak. Right: The magnetic field orientation dependence of the 003 magnetic reflection far below resonance at 5.1 keV (red circles) and the calculated field dependence, assuming spin-only scattering (green). Insert: A schematic of the experiment showing the rotating magnet assembly and $FeBO_3$ spins.

In order to observe interference between the two scattering processes, XMaS measurements were carried out at the 009 reflection position, where the amplitudes were more similar in magnitude than the 003. A polarization analyzer stage was employed to select only the $\sigma - \pi$ channel, again to maximize interference, since the resonant amplitude is entirely in $\sigma - \pi$, while the magnetic scattering is mixed. The origin of the rotations shown in Fig. 2 are such that $\psi = 0$ and η=0 correspond to the crystallographic (100) axis and field direction lying parallel to $\mathbf{k} + \mathbf{k}'$.

As the major result of the present study was a sign, a great deal of care was taken to ensure consistency of sign conventions, the coordinate systems of measurements and simulations, and the direction of the applied magnetic field. The latter was determined with respect to the Terrestrial field.

The results shown in Fig. 3 correspond to interference between the resonant and magnetic amplitude, taken with two opposite field directions to cause a reversal of the magnetic amplitude between scans. One can see a small but clear jump in the energy of the resonant scattering peak as the magnetic field is rotated by 180°, causing the sign of the magnetic scattering, which is given by a projection of the magnetic structure factor in Eqn. 8, to reverse. Such a jump can be understood in terms of constructive/destructive interference between resonant and magnetic scattering on the low/high energy side of the resonance. The direction of the jump gives the phase of the magnetic scattering. The phase of the magnetic scattering gives the sign of the DM interaction. We find that the the magnetic twist follows the twist in the intermediate oxygen atoms in the planes between the iron planes, as depicted in Fig. 1.

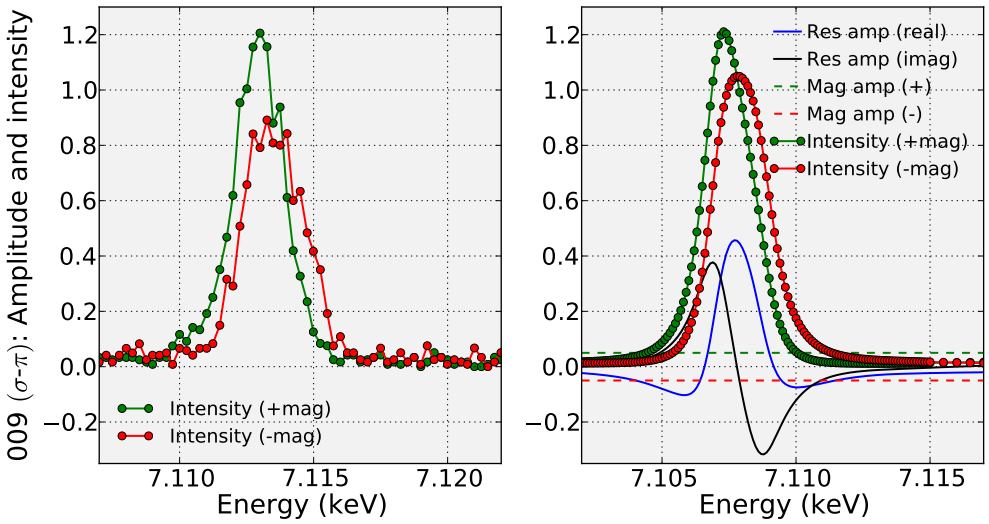

Figure 3. The measured (left) and simulated (right) 009 diffraction intensity close to resonance with the magnetic field applied in two opposite directions to reveal a 'jump' in the resonance energy. Simulations based on the FDMNES program [8] show how the direction of the jump depends on the phase of the magnetic scattering, which in turn depends on the sign of the DM vector. The jump is caused by interference between the antisymmetric imaginary (black line) part of the resonant scattering amplitude - the result of a superposition of two very close resonances of almost equal amplitude but opposite sign - and the purely imaginary magnetic scattering (dashed lines).

5. Conclusions

We have studied the DM interaction in $FeBO_3$, using a variety of techniques to determine its axis, strength and sign. The latter represents the first use of a novel interference technique. These results provide a very sensitive test for the development of predictive theories that can be applied to a range of phenomena including weak ferromagnetism, magnetoelectric materials and skyrmion states.

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